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Thermal and cold flow properties of bio-derived rejuvenators and their impact on the properties of rejuvenated asphalt binders

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Abstract

Rejuvenators are widely used to improve the properties of asphalt binders particularly low temperature and fatigue cracking behavior. Rejuvenators vary significantly in terms of their physical properties and chemical composition. The nature of the interaction between the rejuvenators and the base asphalt binders is very complex and an extensive study into the chemical and thermal properties of the rejuvenators and how they impact the rheological properties of rejuvenated binders is of paramount importance. In this research, a neat PG58-28 binder is rejuvenated with three different materials produced from soybean oil at a dosage of 6% by total weight of binder. The rheological properties of the control and rejuvenated binders are assessed using performance grades showing a drop in both the critical low and high temperature grades with rejuvenation. The oxidative stability of the rejuvenators as well as the rejuvenated binders is studied using thermogravimetric analysis (TGA). The crystallization and melting points of the rejuvenators are observed using differential scanning calorimetry (DSC). DSC is also used to examine the glass transition temperatures of the control and rejuvenated binders. The TGA results showed one of the rejuvenators to be susceptible to oxidation which agreed with the rolling thin film oven (RTFO) mass loss results. The glass transition temperature of the rejuvenated binders decreased denoting improved low temperature cracking properties in line with the performance grade results.

Keywords

Rejuvenators, Thermogravimetric analysis, Differential Scanning Calorimetry, Glass transition temperature, Oxidative stability

Disciplines

Chemical Engineering | Civil Engineering | Thermodynamics

Comments

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Thermal and cold flow properties of bio-derived rejuvenators and their impact on the properties of rejuvenated asphalt binders

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Highlights

- Three soybean-derived rejuvenators were added to a neat binder.
- The thermal properties of the rejuvenators were studied using DSC and TGA.
- The thermal properties of the rejuvenators can be related to the rheological changes in the binder
- The rejuvenators behaved differently even though they were derived from same source

Abstract

Rejuvenators are widely used to improve the properties of asphalt binders particularly low temperature and fatigue cracking behavior. Rejuvenators vary significantly in terms of their physical properties and chemical composition. The nature of the interaction between the rejuvenators and the base asphalt binders is very complex and an extensive study into the chemical and thermal properties of the rejuvenators and how they impact the rheological properties of rejuvenated binders is of paramount importance. In this research, a neat PG58-28 binder is rejuvenated with three different materials produced from soybean oil at a dosage of 6% by total weight of binder. The rheological properties of the control and rejuvenated binders are assessed using performance grades showing a drop in both the critical low and high temperature grades with rejuvenation. The oxidative stability of the rejuvenators as well as the rejuvenated binders is studied using thermogravimetric analysis (TGA). The crystallization and melting points of the rejuvenators are observed using differential scanning calorimetry (DSC). DSC is also used to examine the glass transition temperatures of the control and rejuvenated binders. The TGA results showed one of the rejuvenators to be susceptible to oxidation which agreed with the rolling thin film oven (RTFO) mass loss results. The glass transition temperature of the rejuvenated binders decreased denoting improved low temperature cracking properties in line with the performance grade results.

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1.Introduction

Several research efforts are underway to assess the effect of rejuvenators on asphalt binders. Numerous studies have reported that rejuvenators enhance the low temperature cracking and fatigue properties of binders (Elseifi, Mohammad and Cooper III 2011, Elkashef and Williams 2017, Cavalli et al. 2018, Gucalon et al. 2018). Rejuvenators can also reduce the rutting resistance of binders by lowering their critical high temperature performance grade (Shen, Amirkhanian and Tang 2007). The use of bio-derived rejuvenators was introduced as an environmental friendly and safe alternative to petroleum-derived rejuvenators, particularly those containing polar aromatic constituents which have been identified as a health hazard (Hajj et al. 2013). Rejuvenators derived from distilled tall oil, cotton seed oil, vegetable oil, and soybean oil were used successfully to modify asphalt (Chen et al. 2014, Zaumanis, Mallick and Frank 2015, Elkashef et al. 2017b). In a recent study, six different rejuvenators including distilled tall oil, waste vegetable oil, and waste engine oil were used to rejuvenate reclaimed asphalt pavement (RAP) binders (Zaumanis et al. 2014). The study investigated the effect of the rejuvenators on both the high and low temperature asphalt binder grades. It was shown that bio-derived rejuvenators had a more significant effect on the low temperature grade compared to petroleum-based rejuvenators. Another study used a soybean oil based rejuvenator to modify both a neat and a polymer modified asphalt binders, where the extent of modification was found to be dependent on the type of binder (Elkashef et al. 2017a).

The chemical and physical properties of rejuvenators vary significantly. It is believed that the chemical compatibility between the rejuvenator and the binder affects the degree of effectiveness of the rejuvenator (Alavi et al. 2015, Elkashef et al. 2017a). Due to this complex interaction between rejuvenators and asphalt binders, it is essential to fully characterize rejuvenated binders from, not only a rheological perspective, but also with regards to their chemical and thermal properties. Thermogravimetry is used to determine both the thermal and oxidative stability of asphalt binders. Thermogravimetric analysis (TGA) measurements detect the mass loss of a sample with temperature under a controlled environment. Thermal stability studies involve using nitrogen to allow the sample to undergo thermal decomposition producing lightweight volatile components, whereas oxidative stability studies are performed under oxygen or air to allow for combustion to occur. A thermal stability study using nitrogen was previously conducted to characterize asphalt binders with varying contents of asphaltenes (Firoozifar, Foroutan and Foroutan 2011). The decomposition temperature was noted to be higher for asphalt binders containing higher asphaltene content. Another study utilized TGA to assess the stability of re-refined vacuum tower bottoms (RVTB) where both nitrogen and air were used as purge gases (Wielinski et al. 2015). Nitrogen gas was initially introduced until a temperature of 600ºC. The purge gas was then switched to air and the temperature was increased to 800ºC to burn off any remaining residue. The study verified the stability of the binders blended with 9% RVTB. TGA was also used to assess the thermal stability of styrene-butadiene-styrene modified binders (Ahmedzade, Tigdemir and Kalyoncuoglu 2007). TGA can also be coupled with mass spectrometry (TGA-MS) and Fourier-transform infrared (TGA-FTIR) to study the chemical structure of evolved gases (de Sá et al. 2015, Elkashef, Williams and Cochran 2017c). TGA-MS was used to assess chemical changes in aged binders heated to a temperature of 900ºC under a flow of argon gas (de Sá et al. 2015). TGA-FTIR was used to study rejuvenated reclaimed asphalt binders and assess the rate of mass loss of the rejuvenator with heating (Elkashef et al. 2017c).

Differential scanning calorimetry (DSC) measures the heat flow into and out of a sample relative to a reference. DSC is used to obtain information regarding the glass transition temperature of asphalt binders as well as identify events related to melting and crystallization of asphalt fractions. The significance of the glass transition temperature is that it indicates distinct changes in properties such as shear modulus, specific heat, and the expansion coefficient. The glass transition temperature was shown to be related to the Fraass brittle point which is an estimate of the temperature at which the binder exhibits brittle properties (Claudy et al. 1992). A Strategic Highway Research Program (SHRP) studied the effect of aging in addition to cooling and heating rates on asphalt fractions(Harrison, Wang and Hsu 1992). It was shown that the glass transition region, marked by an increase in heat capacity, typically extends over a wide range of temperatures between -60ºC and 0ºC. The results of the study also indicated that different asphalts show different melting peaks however a correlation between the asphalt composition and the location and intensity of these peaks could not be established. Another comprehensive study that included over 70 different asphalt binders from different origins and different grades revealed that the glass transition region is observed at low temperatures between -50ºC and -10ºC (Planche et al. 1998). Exothermic and endothermic peaks occurred following the glass transition temperature denoting crystallization and melting of asphalt fractions, respectively. Crystallization upon heating takes place in species which could not crystalize during cooling due to limited mobility (Claudy et al. 1998). Asphalt binders containing waxes have also exhibited endothermic peaks associated with the melting of wax(Lu and Redelius 2007). The occurrence of these melting and crystallization events sometimes perturbs the glass transition region and the use of modulated DSC can help better isolate these events (Gill, Sauerbrunn and Reading 1993). A modulated DSC uses an oscillating sinusoidal temperature program which is superimposed on the linear heating or cooling program typically applied in regular DSC. Such temperature program allows reversible thermal events, namely glass transition, to be separated from irreversible events, namely crystallization and melting (Usmani 1997). The modulated DSC method was used by several studies to fully characterize the exothermic and endothermic events associated with waxes and other asphalt constituents and modifiers (Qin et al. 2014, Lei, Bahia and Yi-qiu 2015). The glass transition temperature is a fundamental property of the material but measured values are sensitive to the thermal history of the material as well as the cooling and heating rates (Usmani 1997). It is thus important to anneal the asphalt binders at high temperature before testing to erase thermal history, and to maintain the same cooling and heating rates so that a valid comparison between the binders can be made. Preheating of the asphalt binder is also important to remove any polar associations that are believed to exist between the asphalt molecules at room temperature. These polar associations can result in exothermic peaks during the heating cycle (Wei et al. 1996).

2. Materials and Methods

A neat PG58-28 was used in this study as the control binder. Three different rejuvenators produced from crude soybean oil were added to the control binder at a dosage of 6% by weight of the binder. The performance grades of the control and rejuvenated binders were determined using a dynamic shear rheometer (DSR) and bending beam rheometer (BBR) testing as per AASHTO T315 and AASHTO T313, respectively. The rolling thin film oven (RTFO) procedure was used to simulate short-term aging of the binders according to ASTM D2872 at 163ºC for 85 minutes. The RTFO-aged binders were long-term aged in a pressure aging vessel (PAV) as per ASTM D6521 for 20 hours at 100ºC and 2.1 MPa, prior to testing them using the bending beam rheometer (BBR) to determine their critical low temperature.

Thermogravimetric analysis (TGA) was utilized to assess the oxidative stability of the rejuvenators and the rejuvenated binders using a Netzsch STA449 F1 instrument. Oxygen was used as the purge gas at a flow rate of 60 ml/min. The use of oxygen allows combustion of the sample to take place as would normally occur in the presence of air. Prior to starting the analysis, an evacuation and fill cycle was first conducted to ensure that any existing gases in the furnace are completely removed prior to introducing oxygen. Samples of the rejuvenators and rejuvenated binders weighing about 5-8 mg were placed in alumina crucibles with pinhole lids. A reference empty alumina crucible was used to account for buoyancy effects due to the purge gas and thermal effects on the balance. The initial sample masses were determined using an internal balance. The internal balance also recorded mass change in the sample with temperature. The samples were equilibrated at 80ºC for 4 minutes before the temperature was ramped up to 800ºC at a rate of 20ºC/minute.

A DSC was used to examine the crystallization and melting points of the different rejuvenators. The effect of the rejuvenators on the glass transition temperature of the rejuvenated binders was also studied using DSC. The DSC measurements were made using a PerkinElmer DSC4000 connected to a cooling accessory that allows measurements to be made at very low temperatures. Hermetically sealed aluminum pans are used which provide an airtight enclosed atmosphere. All samples were run under a nitrogen purge gas flowing at 20 ml/min. To analyze the control and rejuvenated asphalt binders, samples weighing between 5-8 mg were used. The samples were heated to 120ºC for 20 minutes prior to being cooled down at a rate of 10ºC/min to -50ºC. The sample was held at -50ºC for 10 minutes before it was heated up to 60ºC at 10ºC/min. Even though the cooling rate was set to 10ºC/minute, the temperature of the samples followed an exponentially decaying rate where it became more and more difficult to cool the samples at lower temperatures. The actual cooling cycle took about 30 minutes to bring down the sample temperature to -50ºC. Only the heating cycle was reported and used to determine the glass transition temperature of the binders. The temperature program used for analyzing the rejuvenators started by holding the sample at 40ºC for 2 minutes before cooling it down to -50ºC at a rate of 10ºC/minute. The sample was equilibrated at -50ºC for 5 minutes and then heated up to 40ºC at 10ºC/minute. The cooling cycle was used to examine the crystallization process while the heating cycle was used to examine the melting process.

3. Results and Discussion

3.1 Performance Grades

The performance grades of the control P58-28 binder and the rejuvenated binders containing the three different rejuvenators were determined as shown in Table 1. The performance grade of a binder determines its working range, where the PG symbol is followed by both the critical high temperature and the critical low temperature. All three rejuvenators had the same effect of reducing the overall performance grade of the control binder from a PG58-28 to a PG46-34. There were however some variations in the continuous high temperature and low temperature grades between the three rejuvenated binders. The critical high temperature grade of all three rejuvenated binders appeared to be controlled by the RTFO-aged condition. For the RTFO-aged rejuvenated binders, the continuous high temperature grades reported for all three binders were very close ranging from 47.7ºC to 48.0ºC. As for the unaged rejuvenated binders, the continuous high temperature grade of the R1 rejuvenated binder was slightly lower at 45.8ºC compared to the R2 and R3 rejuvenated binders at 47.3ºC and 47.2ºC, respectively. These results indicate that the R1 rejuvenator had a greater effect on the continuous high temperature grade of the unaged binder as compared to both R2 and R3. This noted effect of the R1 rejuvenator on the unaged binder however was not maintained after RTFO-aging and all three rejuvenators appeared to affect the RTFO-aged binder to similar extents. This reduced effect of the R1 rejuvenator with RTFO-aging could be attributed to its mass loss. The R1 rejuvenated binder showed a significant mass loss with RTFO-aging with an average mass loss of 1.3%, compared to an average mass loss of 0.5% for both the R2 and R3 rejuvenated binders.

With respect to the continuous low temperature grade, the R3 rejuvenated binder appeared to slightly outperform the R1 and R2 rejuvenated binders which showed very similar performance. Both R1 and R2 resulted in a drop in the continuous low temperature grade of about 7.7ºC and 7.8ºC, respectively. The effect of the R3 rejuvenator was slightly better where the drop in the continuous low temperature grade was about 9.5ºC.

3.2 Thermogravimetric analysis (TGA)

The results of the oxidative stability analysis of the rejuvenators are shown in Figures 1 and 2. Figure 1 displays the thermogravimetric (TG) curve indicating mass loss with temperature, while Figure 2 is a plot of the rate of mass loss with temperature, referred to as derivative thermogravimetric (DTC) curve. The TG curves show that the rejuvenators react differently under oxygen with increasing temperature. The initial decomposition temperature (IDT), herein arbitrarily defined as the temperature at 2% mass loss, is shown in Table 2. The rejuvenator R2 appears to have the highest IDT at 215ºC, followed by rejuvenator R3 at 179ºC and rejuvenator R1 at 165ºC. The data in Figures 1 and 2 clearly show that even though rejuvenators R3 and R1 have similar IDTs, their rate of decomposition following the initial decomposition stage, is different with R1 exhibiting a much higher mass loss rate.

The DTG curves for all rejuvenators show two distinct peaks. The first peak corresponds to the maximum mass loss occurring due to the thermal oxidation of the main constituents of the rejuvenator whereas the second peak corresponds to the combustion of the remaining char residue. The temperatures corresponding to these two peaks in the DTG curves are listed in Table 2.

From the TG and DTG results, it is obvious that rejuvenator R1 has the poorest (lowest) oxidative stability in terms of both its IDT and its rate of decomposition. These results agree with the findings of the RTFO mass loss which clearly indicated that binders rejuvenated with R1 have considerably higher mass loss. Between the R2 and R3 rejuvenators, R2 rejuvenator has better oxidative stability up to a temperature of 215ºC which corresponds to its IDT. Beyond its IDT, R2 rejuvenator however shows a much higher rate of decomposition compared to R3 rejuvenator which makes the latter more thermally stable at higher temperatures.

TGA was conducted for the three rejuvenated binders as well as the control binder. The TG curves, shown in Figure 3, were compared to assess the effect of the rejuvenators on the oxidative stability of the binders. The IDT, previously defined at 2% mass loss, was obtained as listed in Table 3. The differences between the binders were not considerable at this stage, however the performance of the binder rejuvenated with R2 was very similar to that of the control binder due to the high initial decomposition temperature of the R2 rejuvenator as depicted in Figure 1 above. At temperatures above 340ºC, the binder rejuvenated with R3 showed better oxidative stability compared to the other two rejuvenated binders due to the low rate of mass loss exhibited by rejuvenator R3 at high temperatures. The DTG curves for the control and modified binders are shown in Figure 4. The DTG curves show four peaks at which the rate of mass loss is maximized. The first peak denoting the initial decomposition stage has the least intensity occur around 300ºC. The second and third peaks occur above 300ºC and 400ºC, respectively. The temperatures corresponding to the second and third peaks are listed in Table 3. The peaks corresponding to the R3 rejuvenated binders are slightly shifted towards higher temperatures compared to the other two rejuvenated binders, owing to the low mass loss rate of the R3 rejuvenator. The fourth and final peak occurring above 500ºC is due to burning off the remaining char residue of the binders.

3.3 Differential Scanning Calorimetry (DSC)

The DSC scans for the rejuvenators including both the cooling and heating cycles are shown in Figures 5-7. The crystalization process is marked by exothermic peaks occuring during the cooling cycle whereas the melting process results in endothermic peaks during the heating cycle. For each of the rejuveantors, multiple crystalization and melting peaks are measured indicating that the rejuvantor is made up of several constituents. It is well established that saturated fatty acids crystalize at high temperatures, which makes a higher degree of unsaturation more desirable in terms of low temperature properties through lowering the crystaliztion temperature (Borugadda and Goud 2014). During the cooling cycle, the rejuveantor's constituents crystalizes in order of their level of saturation with saturated fatty acids crystalizing first followed by unsaturated fatty acids. The crystalization temperatures of the rejuveantors can also serve as an indication of their cold flow properties. The cold flow properties can be described by the pour point which is defined in ASTM D-5949 as the temperature at which the sample can flow from a container when tilted. This property can be important in cold regions where sufficient flowabilty of the rejuvenator is required to ensure efficient blending to the binder without excessively heating the blend. R1 rejuvenator started to crystalize around 8^{o}C. Some constituents of the R1 rejuvenator however did not crystalize until it reached a temperature of around -35^{o}C. The saturated compounds in the R2 and R3 rejuveantors crystalized at -0.5 ^{o}C and 3 ^{o}C, respectively. The R2 rejuvantor contained other unsaturated constituents which crystalized over a wide range from -10 ^{o}C to -40^{o}C.

The heating scans showed the melting peaks of the rejuvenators. The melting peaks were much broader than the crystalization peaks. The complete melting of the rejuvenators back to their liquid form did not take place until around a temperature of 20^{o}C.

Figure 8 shows the DSC scans of the heating cycle for the control and rejuvenated binders. A wide glass transition region was noted for all of the binders. A shift in the glass transition region towards lower temperatures occurred for the rejuvenated binders compared to the control binder. Other peaks were noted at temperatures higher than 10^{o}C which could be attributed to wax materials within the asphalt binders.

The glass transition temperature is formally defined as the half vitrification temperature (Baur and Wunderlich 1998). In this research, the reported glass transition temperature was calculated as the temperature at which the heat capacity reaches its midpoint between the glassy and amorphous phases. The glass transition onset temperature marks the beginning of the glass transition region and is estimated as the intersection between the tangent line below the glass transition and the tangent line at the steepest point in the glass transition region (Usmani 1997). A software called Pyris from PerkinElmer® was used to analyze the DSC scans and automatically calculate the glass transition and onset temperatures using the definitions above. Table 4 lists the glass transition temperature (T_g) and glass transition onset temperature for the binders. All rejuvenated binders showed a decrease in their glass transition temperatures and onset temperatures compared to that of the control binder. The reduction in the glass transition temperatures is consistent with the performance grading results which show an improvement in the low temperature properties. The glass transition temperature marks a change from a rubbery phase to a brittle phase. As the glass transition temperature of the binder decreases, its low temperature performance is improved.

Summary and conclusions

In this research, a neat PG58-28 binder was modified using three different rejuvenators produced from soybean oil. The rheological changes brought by the rejuvenation process were assessed through the performance grades of the binders. All three rejuvenators resulted in a drop in both the high and low temperature grade of the control binder. The extent of modification caused by the three rejuvenators was comparable however rejuvenator R3 appeared to have a greater effect on the low temperature grade. The binder rejuvenated with R1 suffered from a higher mass loss.

A study of the oxidative stability of the rejuvenators using thermogravimetric analysis (TGA) revealed the following:

- R1 rejuvenator was highly susceptible to oxidation as evidenced by the high mass loss.
- Rejuvenator R2 had the highest oxidative stability with an initial decomposition temperature of 215°C compared to a decomposition temperature of 165°C and 179°C for rejuvenators R1 and R3, respectively.
- Rejuvenator R3 exhibited the lowest rate of mass loss among all rejuvenators at temperatures beyond around 250°C.
- The TGA curves of the rejuvenated binders showed slight variations from that of the control binder. The initial decomposition temperature of the binders revealed that the R2 rejuvenated binder exhibits slightly higher oxidative stability compared to the other two rejuvenated binders. At temperatures above 340°C, the binder rejuvenated with R3 however showed better oxidative stability owing to the low mass loss rate of the R3 rejuvenator.

The crystallization and melting behavior of the rejuvenators was evaluated using differential scanning calorimetry (DSC) and the following was noted:

- Crystallization was shown to occur in stages where saturated compounds crystalized first at temperatures near and above 0°C followed by unsaturated compounds at low temperatures below -10°C. The melting peaks observed during the heating cycles of the DSC scans were broader than the crystallization peaks and occurred at higher temperatures.

DSC was also used to study the glass transition region and the following observation was made:

- The glass transition region of the control binder was noted to shift towards lower temperatures with the addition of the rejuvenators. The glass transition temperature decreased with rejuvenation in line with the improvement in the low temperature performance grade.

In conclusion, this study revealed that the thermal properties of the rejuvenators, as measured by its oxidative stability and its crystallization and melting peaks, have an impact on the rheological changes in the rejuvenated binders. In the future, further work needs to be done to correlate between the thermal properties of the rejuvenators and its impact on the rheology of the binders.

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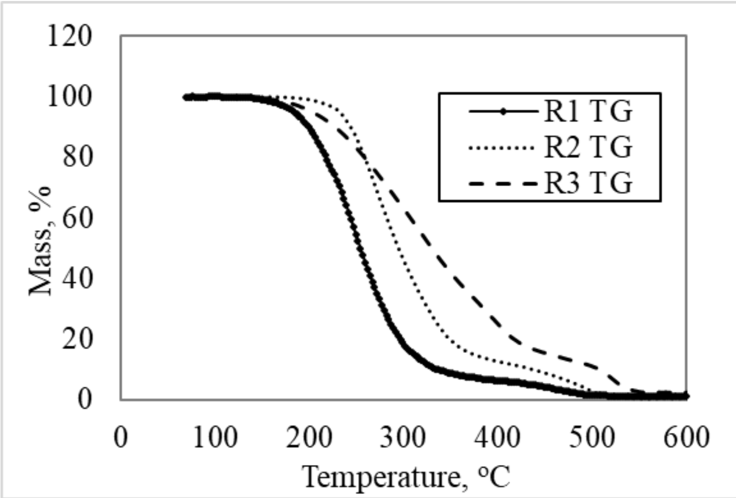

Figure 1: Thermogravimetric curve for rejuvenators

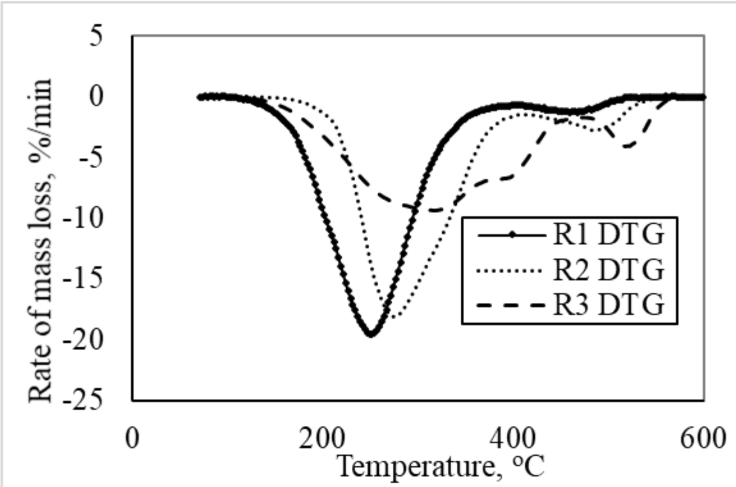

Figure 2: Derivative thermogravimetric curves for rejuvenators

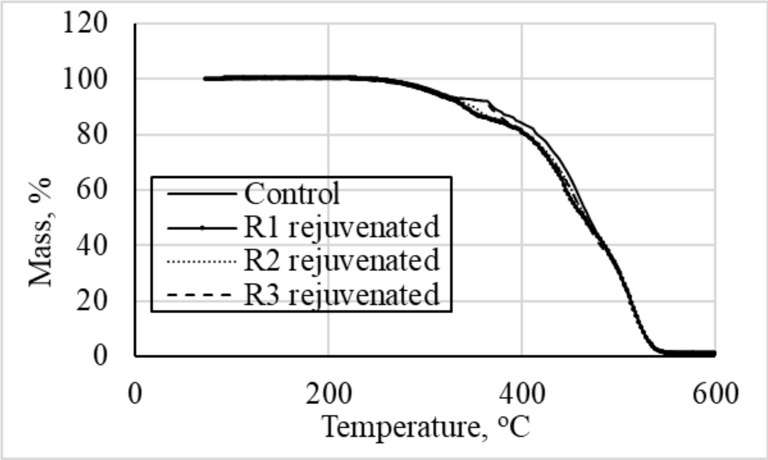

Figure 3: Thermogravimetric curves for all binders

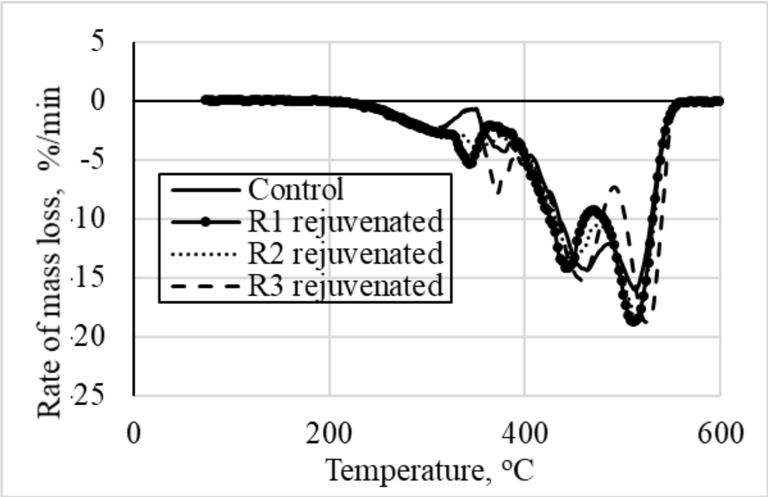

Figure 4: Derivative thermogravimetric curves for all binders

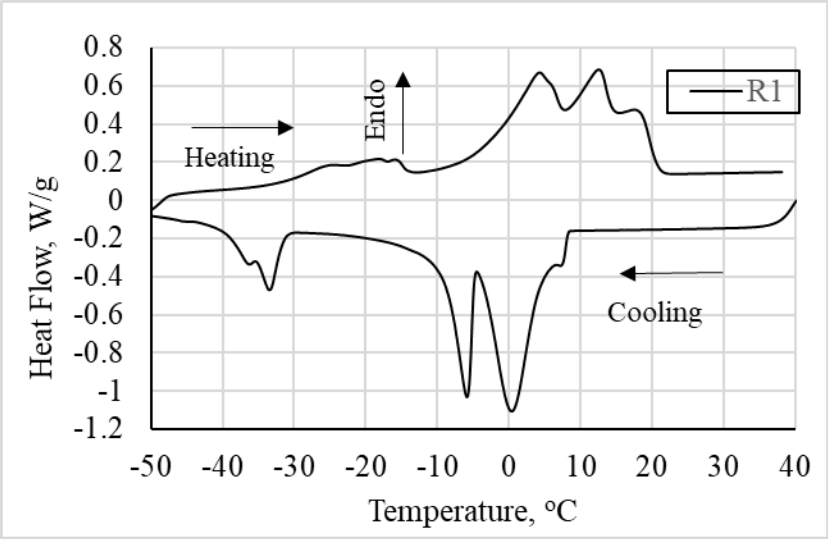

Figure 5: DSC scan for rejuvenator R1

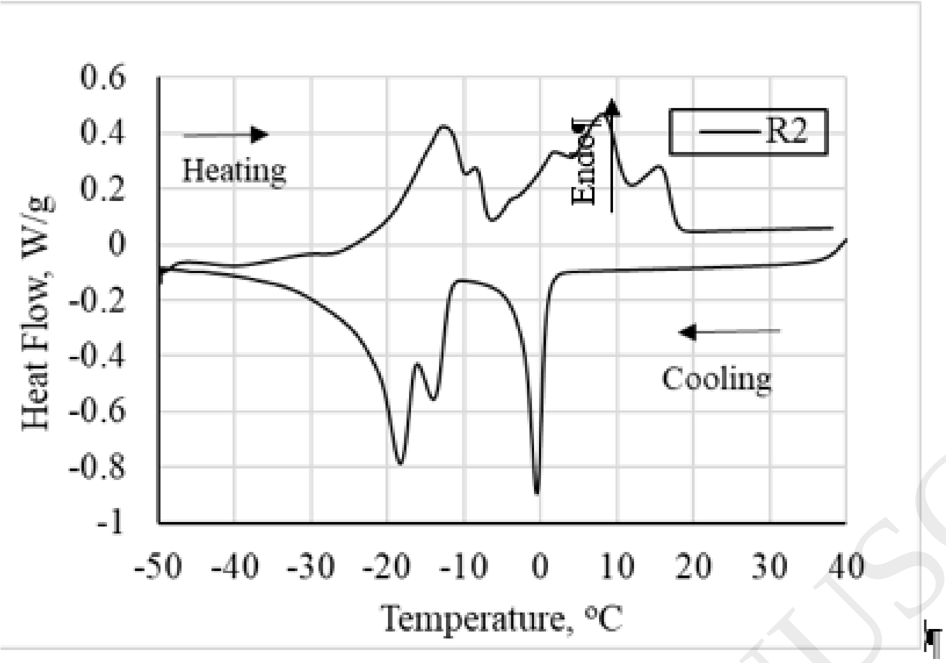

Figure 6: DSC scan for rejuvenator R2

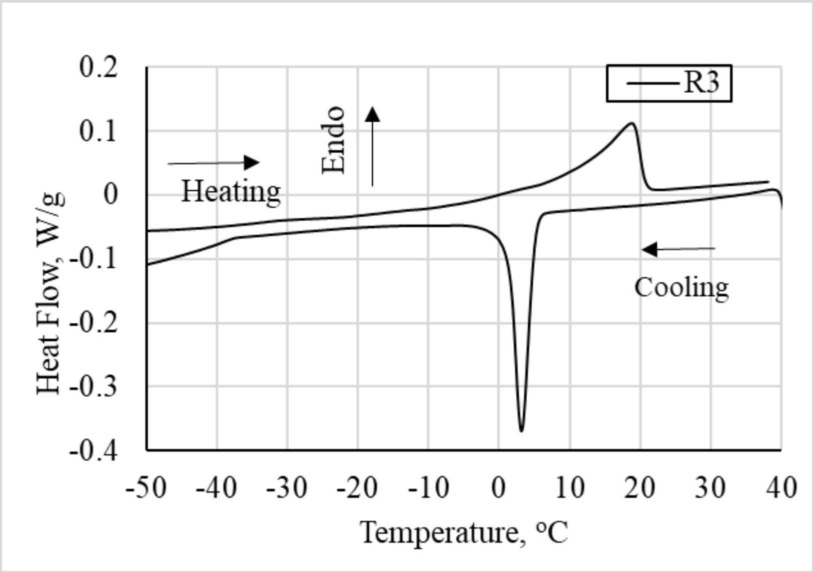

Figure 7: DSC scan for rejuvenator R3

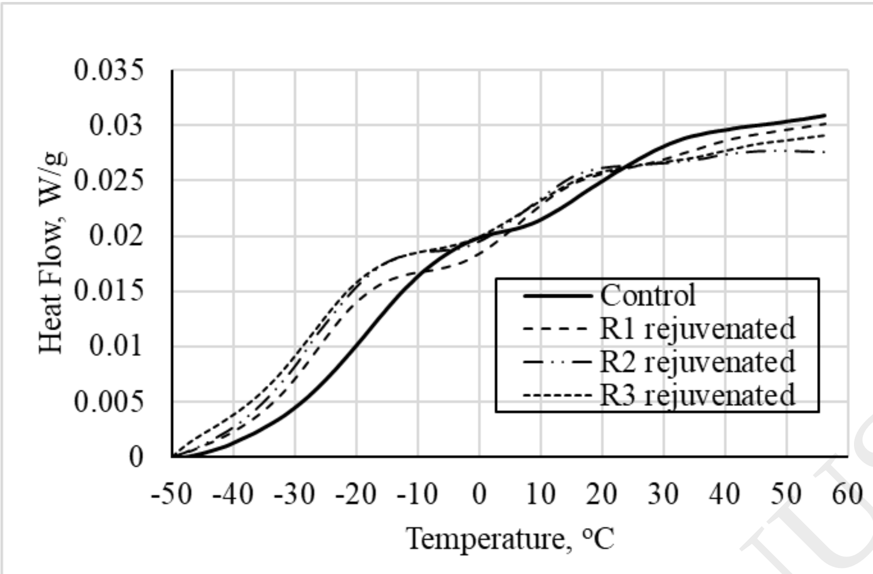

Figure 8: DSC scan of heating cycle

Table 1: Rheological properties of control and modified binders

Binder	PG58-28	PG58-28 + 6% R1	PG58-28 + 6% R2	PG58-28 + 6% R3
Unaged (High Temp.), ^{o}C	60.1	45.8	47.3	47.2
RTFO (High Temp.), ^{o}C	62.5	47.9	47.7	48
PAV (Low Temp.), ^{o}C	-29.9	-37.6	-37.7	-39.4
Performance Grade (PG)	58-28	46-34	46-34	46-34
Mass loss (%)	0.2	1.3	0.5	0.5

Table 2: Thermal characteristics of the rejuvenators

Rejuvenator	R1	R2	R3
Initial Decomposition Temperature, ºC	165	215	179
DTG, 1st peak, ºC	251	275	316
DTG, 2nd peak, ºC	466	483	517

Table 3: Thermal Characteristics of the control and rejuvenated binders

Binder	Control	R1 rejuvenated	R2 rejuvenated	R3 rejuvenated
Initial Decomposition Temperature, ^{o}C	290	280	288	278
DTG, 2nd peak, ^{o}C	378	343	358	370
DTG, 3rd peak, ^{o}C	463	448	451	458

Table 4: Glass transition properties of studied binders

Binder Type	Control	PG58-28 6% R1	PG58-28 6% R2	PG58-28 6% R3
Tg, ºC	-20.8	-28.2	-28.6	-29.1
Onset, ºC	-35.4	-36.7	-39.9	-40.2